

Conf 910473-2

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INTO A SANDY AQUIFER**

CONF-910473--2

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"PREPRINT EXTENDED ABSTRACT"
Presented Before the Division of Environmental Chemistry
American Chemical Society
Atlanta, GA April 14-19, 1991

IRON DYNAMICS DURING INJECTION OF DISSOLVED ORGANIC CARBON INTO A SANDY AQUIFER

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The dynamics of dissolved, colloidal, and solid-phase iron were examined during a forced-gradient field experiment in Georgetown, South Carolina, in the summer of 1990. The experiment involved injection of 80,000 L of oxygenated water containing high levels of dissolved organic carbon (66 mg/L DOC) into a sandy aquifer. Iron dynamics were followed for 2 weeks in three saturated horizons at sampling wells located 1.5 m (A wells) and 3 m (B wells) from the injection well. The initial oxidation/reduction potential of the aquifer favored Fe(II) in the iron-rich groundwater.

As oxygen-rich water was introduced into the groundwater, the redox potential was expected to increase. The impacts of the changing redox potential on iron dynamics were hypothesized to be as follows: (1) Fe(II) may decrease and Fe(III) may increase due to oxidation, but otherwise Fe(II) may be mobile and conservative. (2) Fe(III) is mostly in the ferric oxide/hydroxide colloidal fraction, that is, the ferric fraction may be found predominantly in sizes $> \sim 1$ nm (or > 3000 mol. wt), and the transport of colloidal iron oxide may be limited. (3) Ferric oxide/hydroxide colloids may have positive or near-zero surface charge in the pH range of the groundwater (6.0–7.2). (4) The turbidity of groundwater may increase as a result of the formation of iron colloids.

During the course of injection, dissolved oxygen (DO), pH, iron concentration, DOC concentration, and turbidity were measured. Samples were also collected for microelectrophoretic mobility measurement (Coulter model: Delsa 440), particle-size analysis [Coulter model: N4MD, based on photon correlation spectrometry (PCS)] and scanning electron microscopic examination (ISI-40). The results from the two sampling wells are summarized briefly.

A1 Well — the sampling well located in the saturated zone closest to the water table and 1.5 m from the injection well.

During the injection period, it was observed that DO substantially increased from 0.1 to 1.5 mg/L and that turbidity increased by a factor of 10 (Figure 1). A comparison of ferric/ferrous concentration and size distribution at the beginning and the end of injection (Figure 2) shows that Fe(III) increased more than 20-fold. Fe(II) in the same period was reduced to one-tenth of its initial value. At the end of the injection (Figure 3), 73% of Fe(III) was retained on a 0.1- μ m filter. Fe(II), however, was mainly in the dissolved form (passing through 3000- and 100,100- mol. wt filters). The organic matter was largely in the < 3000 - mol. wt size range, with about 30% of organic carbon in the range of 3000–100,100 mol. wt.

The electrophoretic mobilities of groundwater particles in the A1 well at the beginning and the end of the DOC injection both showed negative surface potentials (Table 1). The number of groundwater particles increased substantially as indicated by counts per second (CPS), from 8400 CPS at the beginning to 148,000 CPS at the end of the injection. The sizes of the groundwater particles fell into two ranges: one, about 200 nm; the other, $> 3\mu$ m. This bimodal

distribution is in good agreement with observations under a scanning electron microscope (SEM), which showed individual spherical particles of 200 nm and large aggregates of these particles. X-ray analysis of SEM samples indicated the presence of iron on the colloidal particles.

Because the A1 well is close to the water/air interface, moderately high DO content was achieved at the end of the injection (1.5 mg/L). In the presence of oxygen, the Fe(II) is rapidly oxidized, and the half-life is on the order of minutes, as demonstrated in laboratory study (ref.1). The disappearance of Fe(II) and the production of Fe(III) during the injection may be accounted for by the fast oxygenation process.

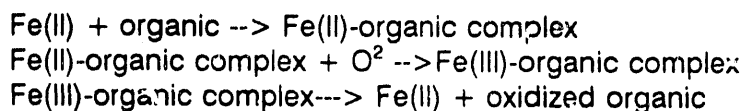
Because Fe(III) hydroxides/oxides are sparingly soluble, precipitation of Fe(III) will follow oxidation. The observation is from SEM and PCS support the existence of colloidal groundwater particles. These colloids are most likely iron colloids because most of the Fe(III) is in the size range $> 0.1 \mu\text{m}$. Colloids of $>0.1 \mu\text{m}$ will be very effective in scattering light and influencing turbidity.

At pH 6.0–7.2, most iron hydroxide/oxide particles will have a positive or neutral charge (ref. 2). The consistently negative surface potential from electrophoretic mobility measurement suggests that iron colloids are associated with anions. Fourier Transform Infrared Spectroscopy analysis on a sample from A1 showed a strong spectrum for $-\text{COO}^-$ (Dr. N. Marley, Argonne National Laboratory, personal communication). Carboxylate bonding to iron oxide has been established by Peck et. al. (ref. 3); hence, the association of iron colloids with organic anions may result in the negative surface potential of particles. The lack of positively charged particles can also be interpreted as follows: because the aquifer material is composed of negatively charged sand, any positively charged iron particles will be preferably retained by the sand. Consequently, the transport of iron colloids would not be possible. However, the increase in Fe(III) is twice as great as the decrease of Fe(II) in the sampling well at the end of the injection, suggesting that transport of iron colloids may be occurring. This apparent transport may be due to the mobilization of the anion-coated iron colloids in the groundwater.

B2 Well — the sampling well located in a slow-flowing zone, 3 m from the injection well.

Both turbidity and DO remained constantly low during the DOC injection (Figure 1). A comparison of Fe(II) and Fe(III) distribution at the beginning and the end of the DOC injection shows that the Fe(III) concentration was doubled, whereas Fe(II) increased slightly (Figure 2). At the end of the injection, 80% of Fe(III) and 100% of Fe(II) were <3000 mol. wt. The organic matter was distributed mainly in the $<100,000$ mol. wt. range, in which 62% were <3000 mol. wt.

The electrophoretic mobilities of groundwater particles showed only negative surface potentials. An increase in the CPS was observed over the injection period. On SEM, large floc was identified, and x-ray analysis of the 200-nm particles indicated the presence of iron. The B2 well lies in a zone of slow groundwater movement. DO injected with the DOC water may be used up in the oxidation process before reaching B2. Alternatively, DO may be taken up from microbial activities. These may cause the low DO during the injection. Under low-DO and high-DOC conditions, Fe(II) oxidation is limited. Fe(II)-Fe(III) may act as a catalyst for oxidation of organic material (ref. 4), as explained by the following reactions:



The observation of high ferrous concentration throughout the injection may be due to a slow oxidation of Fe(II) in comparison to the Fe(II) reduction by organic matter. Alternatively, bacteria may use Fe(III) as an oxidizing agent in the breakdown of organic carbon, producing Fe(II).

In the B2 well, levels of both Fe(II) and Fe(III) increased during the injection, but most of

the iron was <3000 mol. wt. This low-molecular-weight distribution may be accounted for by the high DOC which enhances iron colloid dissolution and the formation of complexes of low-molecular-weight DOC with the Fe(III), rather than by the Fe(III) precipitates observed in the A1 well. The very low concentration of Fe(III) of greater than 0.1- μ m size results in little intensity of light scattering and is consistent with the observed low turbidity. The formation of large aggregates as identified in SEM may be a result of the bridging between organic matter and iron colloids (>0.1 μ m). It is concluded that oxidation of Fe(II) to Fe(III), followed by precipitation of ferric hydroxide/oxide, accounts for the turbidity increase in the A1 well. The interaction of DOC and iron oxide particles alters the electric charge potential of the colloid surface. DOC thereby stabilizes iron colloids and allows the transport of inorganic colloids in porous media.

In the B2 well, oxidation of Fe(II) is slow because of low DO, thus maintaining a steady-state Fe(II) concentration. Increased concentrations of both Fe(II) and Fe(III) are postulated as being due to the DOC- enhancing iron colloid dissolution and the formation of iron-organic complexes rather than to the precipitation of Fe(III) observed in the A1 well.

References:

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2. James, R. O., and G. A. Parks. "Characterization of Aqueous Colloids by Their Electrical Double-Layer and Intrinsic Surface Chemical Properties." *Surface and Colloid Science*, Plenum, New York, 12. 1982.
3. Peck, A. S., L. H. Raby, and M. E. Wadsworth. "An Infrared Study of the Flotation of Hematite with Oleic Acid and Sodium Oleate." *Trans. AIME* 235, 301. 1966.
4. Stumm, W., and J. J. Morgan. *Aquatic Chemistry*; Wiley and Sons: New York, 1981; Chapter 7.

Figure and Table Captions:

- Figure 1: Changes in dissolved oxygen and turbidity during injection for the A1 and B2 sampling wells. Injection started on 7/10/90 and ended on 7/23/90.
- Figure 2: Changes in concentration and size distribution of Fe(II) and Fe(III) during injection of organic-rich, oxygenated water for the A1 and B2 wells. On the x-coordinate, 0 indicates the beginning of the injection, and 312 is the ending hour of the injection.
- Figure 3: Size distribution of Fe(II), Fe(III), and dissolved organic carbon at the end of injection. Amicon hollow-fiber filters were used for each size cut.
- Table 1: Comparison of particle-size distribution and electrophoretic mobility at the beginning and the end of injection for the A1 B2 Wells.

Research supported by the Subsurface Science Program, Ecological Research Division, U.S. Department of Energy, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

Table 1

OUTPUT FROM PHOTON CORRELATION SPECTROMETRY
(Coulter N4MD)

		d (nm), %	d (nm), %	d (nm), %	CPS*
PRE-INJECTION	A1	3, 6%	214, 43%	2400, 52%	8.7±0.7
	B2	15, 1%	249, 36%	3000, 70%	18.2±0.8
END OF INJECTION	A1		286, 100%	>3000, 3%	148.0±4.1
	B2		396, 26%	3000, 7%	269.8±18.5

* counts per second (1000/sec)

OUTPUT FORM MICRO-ELECTROPHORESIS
(Coulter Delsa 440)

PRE-INJECTION	A1	-23.4 ± 4 mV
	B2	-24.0 ± 3 mV
END OF INJECTION	A1	-13.6 ± 9.1
	B2	-15.9 ± 8.9

CPRL-OWB 882-1870

Fig. 1

CHANGES IN D.O. AND TURBIDITY
DURING DOC INJECTION

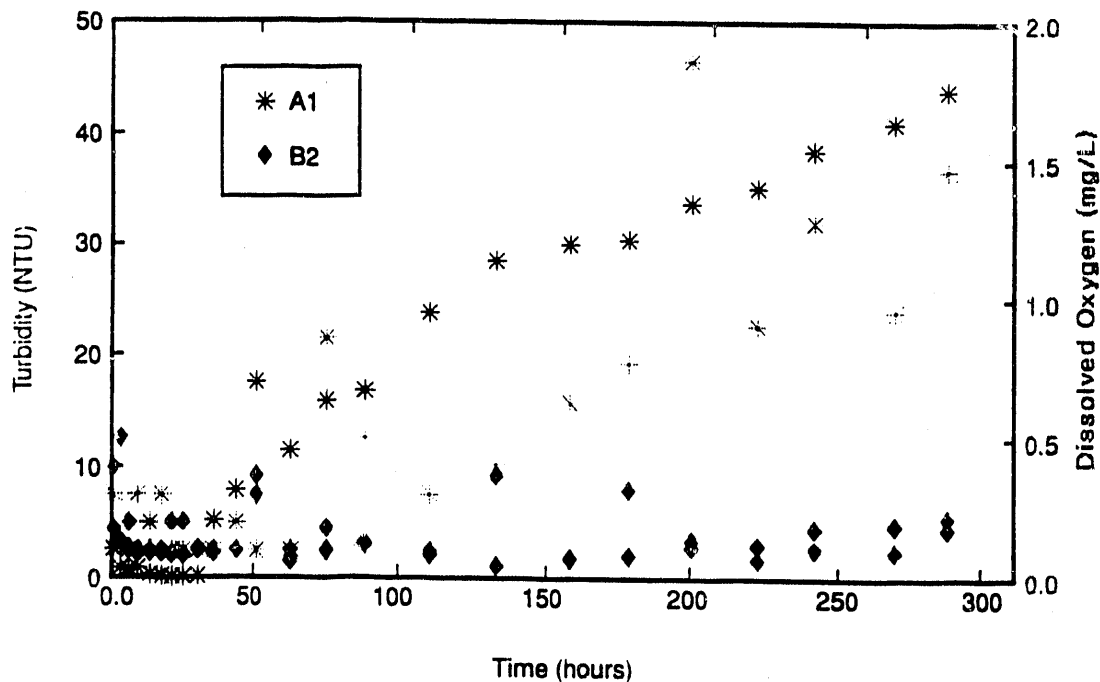


Fig 2 **CHANGES IN CONCENTRATION AND SIZE OF Fe²⁺ AND Fe³⁺ DURING DOC INJECTION**

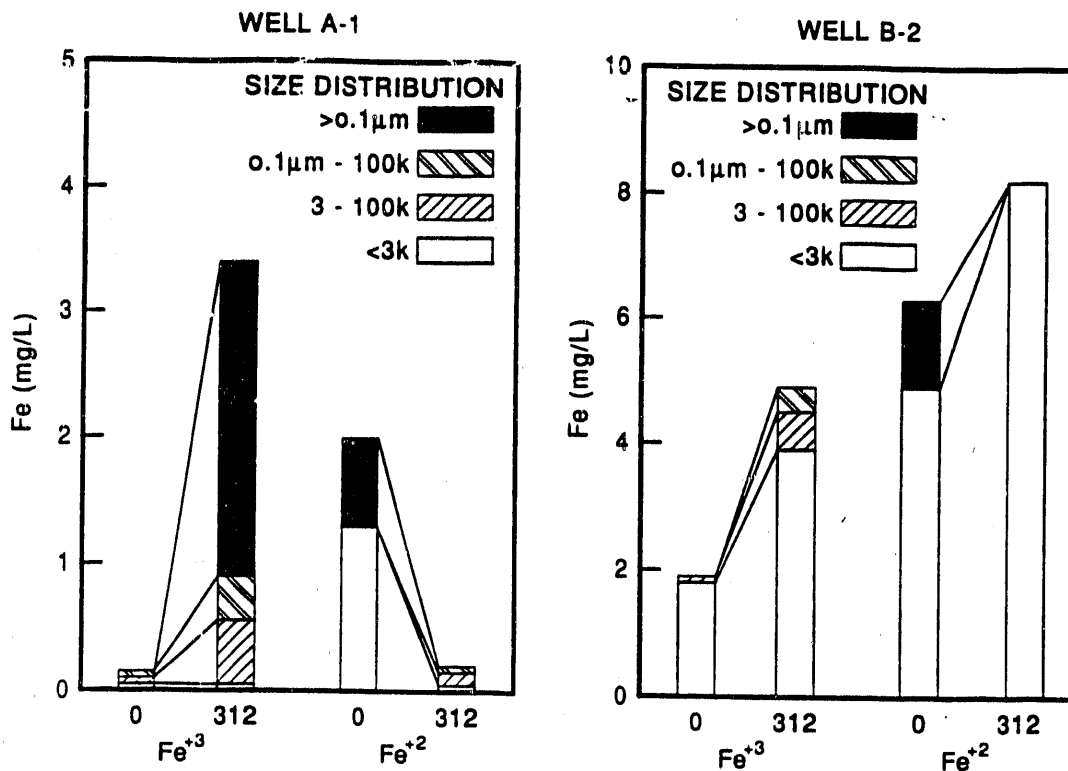
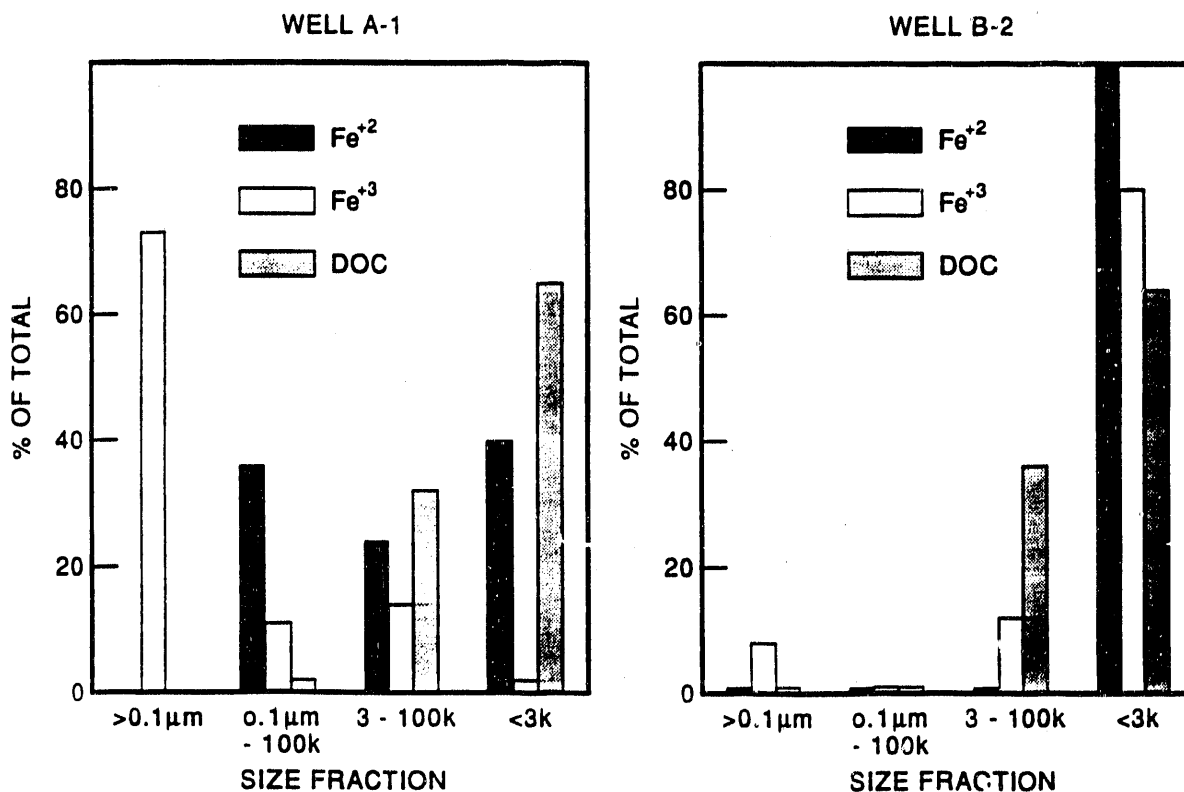


Fig 3 **SIZE DISTRIBUTION OF Fe²⁺, Fe³⁺ AND DOC AT END OF DOC INJECTION**



$$d[\text{Fe(II)}]/dt = -k_H[\text{O}_2(\text{aq})][\text{Fe(II)}]/[\text{H}^+]^2$$

where $k_H = 3 \times 10^{-12}$ moles/liter-min

accordingly, the half time of oxygenation is

$$t_{1/2} = 0.69[\text{H}^+]^2 / k_H[\text{O}_2(\text{aq})]$$

at pH 6.4, $t_{1/2} = 117$ min, if $[\text{O}_2(\text{aq})] = 0.1$ ppm

8 min,	1.5 ppm
1.5 min,	8.0 ppm

END

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